



A comparison between catalytic ozonation and activated carbon adsorption/ozone-regeneration processes for wastewater treatment

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ABSTRACT

Two methods based on the use of granular activated carbon (GAC) and ozone to remove organic compounds from water have been investigated. Both methods have been applied to degrade an aqueous solution of gallic acid and a secondary effluent from a wastewater treatment plant (WWTP). One of the methods, namely catalytic ozonation, implies simultaneous ozonation and adsorption onto GAC. This process takes advantage of the oxidizing power of ozone and the adsorption capacity of GAC but also of the catalytic transformation of ozone into secondary oxidants on the GAC surface. The efficiency of catalytic ozonation was compared to those of single adsorption and single ozonation. It was found that the catalytic process highly improves the conversion of total organic carbon (TOC) and makes a more efficient use of ozone than the single ozonation process. To illustrate the reusability of the catalyst, the GAC was reused four times through a series of consecutive experiments. No loss of catalytic activity was observed when treating the WWTP effluent but some deactivation could be appreciated when treating the aqueous solution of gallic acid. This deactivation could be attributed to some porosity destruction and surface oxidation produced as a result of reactions of aqueous ozone on the GAC surface. The other method investigated is an adsorption-regeneration process (namely GAC/O₃-regeneration) that comprises two steps: dynamic adsorption onto GAC and further regeneration of the spent GAC with gaseous ozone. The adsorption stage of the GAC/O₃-regeneration experiments was carried out in a continuous flow adsorption column and breakthrough curves were obtained. It was observed that the GAC used in this work adsorbed gallic acid very efficiently but exhibited limited capacity to remove chemical oxygen demand (COD) from the WWTP effluent. The optimum ozone dose to regenerate the spent GAC after gallic acid adsorption was found to be about 0.4 g O₃/g GAC, with results showing around 90% regeneration efficiency. As a result of incomplete regeneration, the GAC adsorption capacity progressively decreased with the number of adsorption-regeneration cycles. The GAC/O₃-regeneration method was not successful at treating the WWTP effluent as low adsorption uptake was observed. Moreover, the GAC became damaged after regeneration because of excessive oxidation of its surface.

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1. Introduction

Since Jans and Hoigné [1] the integrated use of ozone and activated carbon has been extensively investigated as an effective advanced oxidation process (AOP) to remove toxic and/or low biodegradable organic compounds from water. The process not only takes advantage of the high adsorption capacity of activated carbon and the high oxidant power of ozone but activated carbon may also transform ozone into secondary oxidants, such as hydroxyl radicals, which can degrade adsorbed and aqueous organic compounds, eventually converting them into carbon dioxide and water (i.e., mineralization). The method is considered as a catalytic ozonation process and it has already been

successfully applied to effectively mineralize a number of aqueous organic compound families [2,3]. Particularly, in a recent series of works, we used this method to degrade some polyphenols typically present in some food-processing wastewaters [4–6]. Textural and chemical properties of the activated carbon surface as well as aqueous pH were found to be key variables of the process.

The removal of many organic compounds from aqueous solution can be easily accomplished by simply adsorption onto activated carbon. However, the suitability of using an activated carbon in an adsorption application depends not only on its uptake capacity but also on the possibility of reusing it several times. The most common available technology to regenerate spent activated carbons is thermal reactivation, though it has some drawbacks as large cost of regeneration facilities, high energy demand and loss of carbon due to oxidation and attrition [7]. Therefore, the research and development of other alternative regeneration methods, which are better to be realized in situ in order to avoid shipment cost, are desirable. In

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this sense, ozone-assisted regeneration of spent activated carbon might be considered. The method implies the adsorption of water pollutants onto activated carbon for a long period of time up to saturation and subsequent *in situ* regeneration of the spent activated carbon by reaction with gaseous ozone during a short time. This method has been already investigated to regenerate activated carbons exhausted with phenol and benzothiazole [8,9].

Considering the ideas addressed above, this research focuses on the comparison between the one-step catalytic ozonation process using granular activated carbon (GAC) as a catalyst and the two-step process consisting of dynamic adsorption onto GAC followed by ozone-assisted regeneration of the spent adsorbent (i.e., GAC/O₃-regeneration). Experiments were conducted on an aqueous solution of gallic acid, a phenolic compound typically present in some food-processing wastewaters, and a secondary effluent taken from a real wastewater treatment plant (WWTP) that treats a mixture of some food-processing and domestic wastewaters. The efficacies of the two processes are assessed in terms of organic compounds mineralization, ozone consumption and GAC reusability.

2. Materials and methods

2.1. Materials

The GAC used in this study, supplied by Sigma–Aldrich, was Darco 12–20 mesh. It is produced by Chemviron Carbon (Belgium) by activation of bituminous coal with steam. The as-received GAC was boiled in distilled water for 1 h, washed repeatedly with ultrapure water (Millipore Milli-Q system), dried at 110 °C for 12 h, and stored in a desiccator at room temperature until use. Textural characterization of GAC samples was accomplished by physisorption of nitrogen at 77 K (Autosorb-1, Quantachrome) and by mercury porosimetry (Autoscan-60, Quantachrome). The BET and α -plot methods were applied to adsorption data to derive the BET surface area and micropore volume (V_1), respectively, whereas the volume of pores of size larger than 3.5 nm (V_2) was obtained from mercury porosimetry measurements. The surface chemistry of GAC samples was analyzed by measuring the concentrations of acidic and basic surface oxygen groups (SOG) following the Boehm's titration method [10]. The point of zero charge (PZC) was analyzed by mass titration [11]. The ash content was determined gravimetrically after combustion of GAC samples in air at 850 °C.

Analytical grade gallic acid (3,4,5-trihydroxybenzoic acid, C₇O₅H₆·H₂O) was purchased from Sigma–Aldrich. Stock solutions of this compound (0.5 g/dm³, COD ~ 540 g/m³, TOC ~ 225 g/m³) were prepared in ultrapure water (Millipore Milli-Q system) and the pH was adjusted to 6 by adding 0.1 M sodium hydroxide. A secondary effluent was collected from a full-scale WWTP located in Almendralejo (Badajoz, Spain). This WWTP receives domestic wastewater as well as wastewater from several food-processing local industry facilities including wineries, distilleries, fruit and vegetable processing industries and olive oil mills. The treatment at the WWTP consists of a screening and primary sedimentation followed by a secondary activated sludge process. To avoid samples heterogeneity linked to seasonal variations of WWTP effluent, all the samples used in this work were collected at the same time in September 2006. Immediately after collection, the samples were shipped to the laboratory, analyzed and kept frozen in PET bottles until being used in experiments. Aqueous pH and conductivity were analyzed by means of a Radiometer Copenhagen pH-meter (HPM82) and Hanna HI9033 conductivity-meter, respectively. Total and suspended solids were measured gravimetrically according to Standard Methods [12]. Chemical oxygen demand (COD) was analyzed by the colorimetric dichromate method using a Dr Lange cuvette test. Biological oxygen demand (BOD₅) was followed by the respirometric method (Oxitop® WTW

system) using an activated sludge sample from the WWTP as inoculum. A TOC-VCSH Shimadzu carbon analyzer was used to measure total organic carbon (TOC), inorganic carbon (IC) and total nitrogen (N_T). Polyphenols were analyzed by the Folin–Ciocalteu method and expressed as equivalent gallic acid concentration [13]. Phosphate and ammonium concentrations were measured using Merck Spectroquant photometric kits. UV absorbance at 254 nm was determined on diluted samples to provide an estimation of the content of olefins and aromatic compounds, which, as a rule, react fast with ozone. A Thermo Spectronic HeXios α spectrophotometer and 1 cm quartz cells were used for the measurements.

2.2. Adsorption isotherms

Equilibrium adsorption isotherms at 25 °C of gallic acid aqueous solution and WWTP effluent on GAC were generated using the bottle point method described elsewhere [14]. Different amounts of GAC were weighted and placed in bottles containing 20 cm³ of either gallic acid aqueous solution or WWTP effluent. The bottles were capped and kept in a shaking thermostatic bath for time enough to achieve adsorption equilibrium. Preliminary experiments showed that equilibrium was reached within less than 1 week. Upon equilibration, the solutions were filtered through 0.45 μ m membranes and analyzed for either gallic acid concentration or COD and TOC. Gallic acid was analyzed by HPLC with a Hewlett Packard series 1110 chromatograph provided with an UV detector set at 280 nm. A Trazer Kromasil-100 (C18; 15 cm \times .4 cm, 5 μ m) column was used, the mobile phase being a mixture of water–acetonitrile–phosphoric acid (90:9:1, v/v/v). COD and TOC were analyzed by the methods cited above. The amount of solute adsorbed per gram of adsorbent at equilibrium (q_e) was derived from the mass-balance equation (1):

$$q_e = \frac{(C_0 - C_e) \cdot V}{w} \quad (1)$$

where C_0 and C_e are the initial and equilibrium aqueous solute concentrations, respectively (i.e., gallic acid concentration, COD or TOC), V is the volume of solution and w stands for the dry mass of GAC.

2.3. Catalytic ozonation experiments

Catalytic ozonation experiments were performed at room temperature in semi-batch mode using an experimental set-up as that depicted in Fig. 1, Part A. The glass bubble column, which had a diameter of 5 cm and length 20 cm, was first loaded with 250 cm³ of either gallic acid aqueous solution or WWTP effluent. Then, a 25 N dm³/h of about 40 mg O₃/dm³ ozone–oxygen mixture was produced in the ozone generator (Sander, model 301.7) and supplied to the bubble column through a porous plate situated at its bottom. The recirculation pump (Masterflex peristaltic, Cole-Parmer Instrument) produced a 2 dm³/h aqueous flow rate through the adsorption column (2 cm i.d.), which held 2 g of GAC unless otherwise specified. The concentration of ozone in the gases entering and leaving the bubble column was monitored with an Anseros Ozomat GM-6000 Pro analyzer. Aqueous samples were withdrawn from the bubble column at different times during the course of each experiment and analyzed for dissolved ozone, gallic acid, COD and TOC. Aqueous ozone concentration was determined by the indigo method [15]. For comparative purposes, blank experiments, either without GAC or without ozone, were also conducted.

2.4. GAC/O₃-regeneration experiments

GAC/O₃-regeneration experiments were carried out at room temperature in an experimental device as that schematically

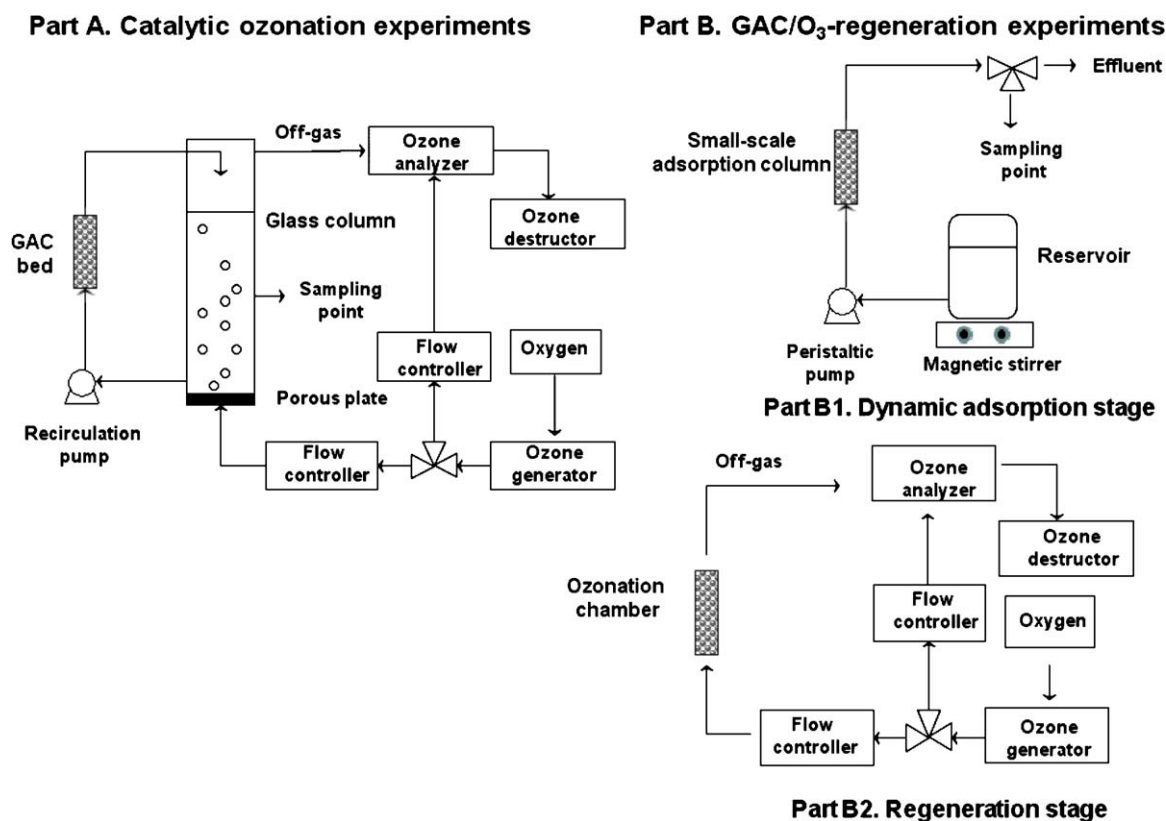


Fig. 1. Schematic diagrams of the experimental devices for catalytic ozonation and GAC/O₃-regeneration processes.

shown in Fig. 1, Part B. A complete treatment cycle involved successive dynamic adsorption and GAC regeneration stages. For the dynamic adsorption stage (see Fig. 1, Part B1), 1 cm³/min flow rate of either gallic acid aqueous solution or WWTP effluent was continuously pumped from the magnetically stirred reservoir to the small-scale adsorption column (2 cm i.d.), which was packed with 2 g of fresh or regenerated GAC. Aqueous samples were taken at different times from the outlet of the column and analyzed for either gallic acid concentration or COD to obtain the breakthrough curve. Once GAC saturation was reached, the pump was stopped and the regeneration stage began. For that, the adsorption column containing the spent GAC was used as an ozonation chamber (see Fig. 1, Part B2). The spent GAC was first partly dried in flowing air and thereafter exposed to a 25 N dm³/h continuous flow of an oxygen–ozone mixture for 1 h. The concentration of ozone in the gaseous streams at the ozonation chamber inlet and outlet was continuously monitored.

To investigate the nature of compounds adsorbed onto GAC, thermal analysis (TGA) of some spent and regenerated samples was carried out by heating about 200 mg of GAC samples in nitrogen flow (9 N m³/h) from room temperature up to 1173 K at a rate of 10 K/min using a Mettler TA-3000 thermobalance. Before TGA, the GAC samples were oven-dried at 110 °C for 2 h.

3. Results and discussion

3.1. Adsorption isotherms onto virgin GAC

Fig. 2A shows the measured isotherm for gallic acid adsorption onto the virgin GAC. It can be included in the type L of the Giles classification which is characterized by an initial rapid uptake followed by the attainment of a plateau [16]. This type of isotherm has been found by a number of researchers when studying the adsorption equilibrium of different phenolic compounds onto

activated carbon [17]. According to the reported in those studies, the adsorption mechanism is most likely due to dispersive forces between π electrons of the aromatic ring of the gallic acid molecule and π electrons of the graphene layers of the activated carbon. From Fig. 2A it is also apparent that the experimental data fit the Langmuir isotherm (Eq. (2)) better than the Freundlich isotherm (Eq. (3)). The parameters of the Langmuir model were estimated from the experimental results of Fig. 2A after applying a non-linear regression method (see the first row of Table 1 for fitting results). It is worthy to note that the maximum adsorption capacity, q_m , and the affinity constant, K_L , were found to be slightly higher than the values reported for the adsorption of gallic acid from aqueous solutions onto other GACs with higher surface areas than that of the used in this work [18,19]. This reveals that this particular GAC (Darco 12–40 mesh) can be a good choice for the removal of gallic acid from aqueous solutions.

$$q_e = q_m \frac{K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (2)$$

$$q_e = K_F \cdot C_e^{1/n} \quad (3)$$

Fig. 2B shows the measured adsorption isotherms for the adsorption of the WWTP secondary effluent onto the virgin GAC.

Table 1

Parameters of the Langmuir isotherm determined at 25 °C for the adsorption of gallic acid onto virgin and some ozone-regenerated GACs.

GAC sample	D_{O_3} (g O ₃ /g GAC)	η_{O_3} (g O ₃ /g TOC)	PR (%)	q_m (mg/g)	K_L (dm ³ /g)	R^2
Virgin	–	–	–	287 ± 6	54 ± 5	0.994
O ₃ -Reg-0.1	0.10	1.44	48.8	192 ± 9	15 ± 2	0.986
O ₃ -Reg-0.2	0.21	3.08	59.9	207 ± 7	23 ± 3	0.987
O ₃ -Reg-0.4	0.42	6.16	87.6	270 ± 10	37 ± 4	0.989
O ₃ -Reg-0.6	0.58	8.53	74.6	268 ± 10	20 ± 2	0.991

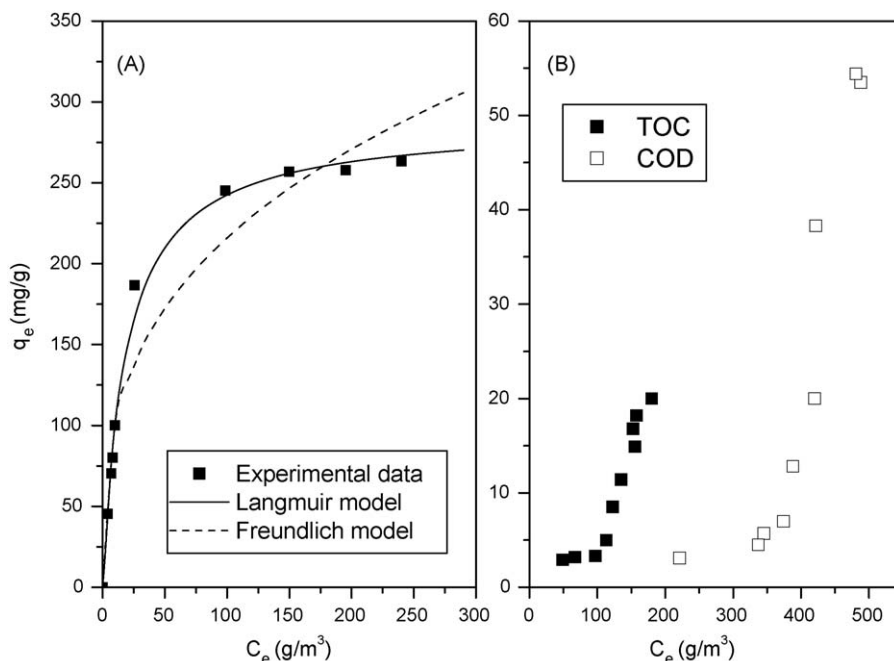


Fig. 2. Adsorption isotherms at 25 °C for gallic acid (A) and WWTP effluent (B) on the virgin GAC.

The isotherms are of type S of the Giles classification [16]. Accordingly, negligible adsorption takes place at low equilibrium COD (or TOC) values but a drastic increase in the adsorption uptake occurs from a critical COD (or TOC) value up to reach the maximum adsorption capacity. This result suggests that such a fraction of the organic matter originally present in the WWTP effluent has not affinity for the GAC surface and it cannot be adsorbed. In fact, it was observed that when the WWTP effluent was brought into contact with the GAC and allowed for equilibrium, no more than 60–70% of COD and TOC could be removed from the effluent regardless of the amount of GAC used.

3.2. Degradation of gallic acid

3.2.1. Catalytic ozonation experiments

Fig. 3 compares some gallic acid concentration and TOC profiles obtained from single ozonation, single adsorption onto GAC and catalytic ozonation experiments. It can be observed that the degradation rate of gallic acid was quite similar when ozonation was carried out in the presence and the absence of GAC but the removal of gallic acid by single adsorption was much slower. Thus, the percentage of gallic acid removed after 2 h of treatment was about 75% by single adsorption whereas by single or catalytic ozonation gallic acid was completely degraded in less than 20 min. However, the removal of TOC by single adsorption was faster than by single ozonation likely because of the accumulation in water of intermediates of the ozone–gallic acid reaction. The most remarkable finding in Fig. 3 is that TOC removal was greatly enhanced by the simultaneous use of ozone and GAC. Thus, gallic acid was almost completely mineralized in 90 min by catalytic ozonation, whereas single ozonation barely produced a 50% TOC removal within this treatment time.

The results of Fig. 3 concur with those previously reported using a slurry reactor and a GAC with surface area around 1000 m²/g [4]. They can be explained on the basis of a fast reaction between ozone and gallic acid but a relatively slow adsorption onto GAC. Accordingly, regardless of the presence of GAC, most of gallic acid reacted with ozone close to the gas–liquid interface in a fast kinetic regime of ozone absorption. The absence of aqueous

ozone during the first 10 min of our experiments (see Fig. 3), when gallic acid still remained in solution, confirms the fast kinetic regime of ozone absorption. As a rule, the ozonation of aqueous gallic acid gives rise to the formation of a number of intermediates (e.g. ketomalonic and oxalic acids) which are difficult to degrade by single ozonation [4]. Because of that, TOC could not be removed to a great extent by single ozonation. It is well known that the O₃/GAC catalytic system produces surface and aqueous free radicals, primarily hydroxyl radicals. These radicals arise mainly from the decomposition of ozone on basic sites of the GAC as chromene and pyrone-like structures and delocalized π electrons of the basal planes [20–22]. Accordingly, as ozone decomposed over GAC, the concentration of ozone in water during the catalytic ozonation experiment was lower than that during the single ozonation

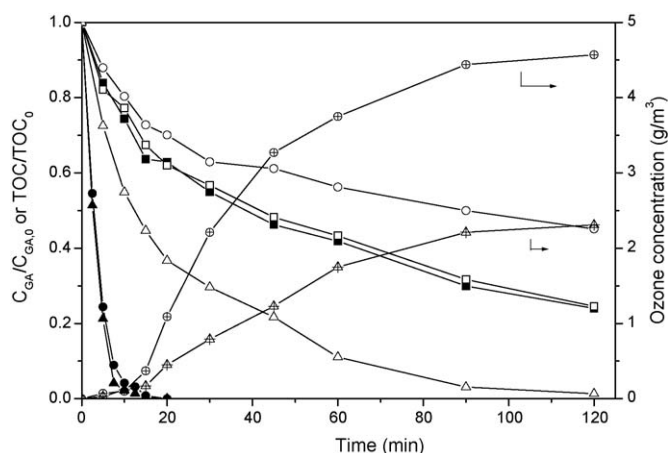


Fig. 3. Degradation of gallic acid by single adsorption, single ozonation and catalytic ozonation experiments. Reaction conditions: $T \approx 20$ °C; pH = 6; aqueous solution volume = 250 cm³; initial gallic acid concentration = 0.5 g/dm³; recirculation flow rate = 2 dm³/h; GAC weight (if applied) = 2 g; gas flow rate = 25 N dm³/h; ozone concentration at the gas inlet = 40 g O₃/m³. Symbols: ■, □, adsorption experiment; ●, ○, single ozonation experiment; ▲, △, catalytic ozonation experiment. Black symbols: gallic acid concentration; open symbols: TOC; +centred symbols: aqueous ozone concentration.

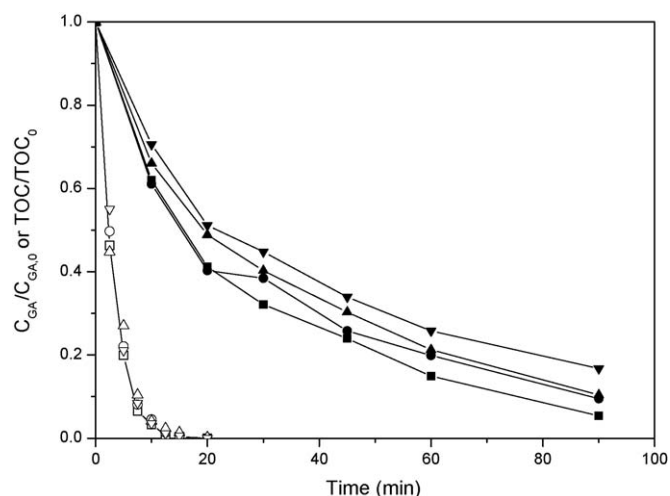


Fig. 4. Effect of the reuse of activated carbon on the degradation of gallic acid (GA) and TOC by consecutive catalytic ozonation experiments. Reaction conditions as in Fig. 3. Symbols: ■, □, Fresh GAC; ●, ○, one-time reused GAC; ▲, △, two-time reused GAC; ▼, ▽, three-time reused GAC. Open symbols: gallic acid concentration; black symbols: TOC.

experiment (see Fig. 3) but hydroxyl radicals generated from ozone decomposition over GAC, unselectively oxidized the organic compounds in solution converting them into CO_2 . As a result, TOC degradation was greatly enhanced by the presence of the GAC.

Eq. (4) was used to estimate an ozone consumption parameter (η_{O_3}), that can be defined as the average amount of ozone consumed per unit mass of TOC removed in a given reaction time (t_f):

$$\eta_{\text{O}_3} = \frac{F_g \cdot \int_0^{t_f} (C_{\text{O}_3,i} - C_{\text{O}_3,o}) \cdot dt}{V \cdot (\text{TOC}_0 - \text{TOC}_{t_f})} \quad (4)$$

where F_g is the gas flow rate; $C_{\text{O}_3,i}$ and $C_{\text{O}_3,o}$ are the concentrations of ozone at the reactor inlet and outlet gas streams, respectively; and V is the volume of aqueous solution. Our results suggest a more efficient use of ozone when the GAC was present. Thus, η_{O_3} decreased from 13.1 g O_3 /g TOC in the single ozonation experiment to 7.4 g O_3 /g TOC in the catalytic ozonation experiment.

To investigate catalyst deactivation behaviour, the GAC was reused in four consecutive catalytic ozonation experiments of degradation of aqueous gallic acid with a run time of 1.5 h. Fig. 4 shows the temporal profiles of normalized gallic acid concentration and TOC for these consecutive experiments. As can be seen from this figure, the removal rate of gallic acid was almost the same in all the experiments while TOC removal rate decreased to some extent after each GAC use. Thus, TOC degradation over the 1.5 h reaction period was about 95% with the fresh GAC and about 85% with the three-time reused. Moreover, η_{O_3} increased from 7.7 g O_3 /g TOC with the fresh GAC to 9.0 g O_3 /g TOC with the three-time reused. These results suggest slow deactivation of the GAC towards ozone transformation into hydroxyl radicals. Deactivation was

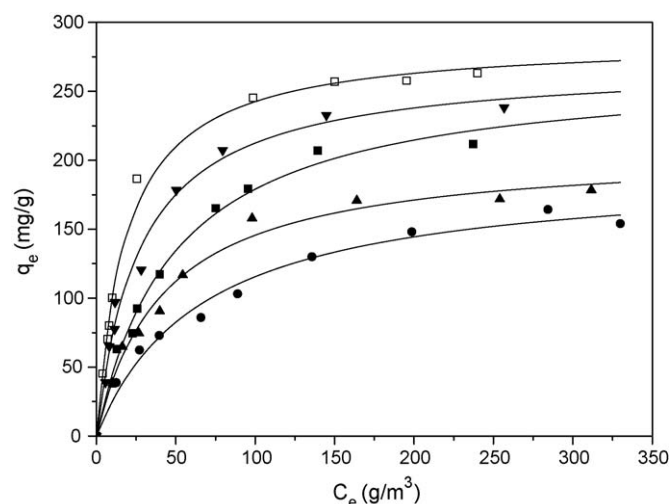


Fig. 5. Adsorption isotherms at 25 °C for gallic acid on the virgin and various ozone-regenerated GACs. Symbols: □, Virgin activated carbon; ●, ○, O_3 -Reg-0.1; ▲, △, O_3 -Reg-0.2; ▼, ▽, O_3 -Reg-0.4; ■, ▽, O_3 -Reg-0.6.

likely due to changes in texture and/or surface chemistry of the GAC produced because of its progressive oxidation upon exposure to ozone [21]. To further clarify this point, a sample of virgin GAC and another of the GAC used in the four consecutive experiments (Used sample 1) were analyzed for some surface properties. From the results of Table 2, it can be seen that surface area, pore volume and ash content of the GAC did not change as significantly but noticeable changes of SOG concentrations and PZC were produced following repetitive experiments. According to data of Table 2, catalytic ozonation led to the removal of basic sites of the GAC such as chromene-like, pyrone-like and delocalized π -electrons of the basal planes and the fixation of acidic SOG such as carboxylic, lactone and hydroxyl groups. As a result of that, PZC decreased to some extent. Given the fact that basic sites are main responsible for ozone transformation into hydroxyl radicals, it can be concluded that the partial deactivation of the GAC towards TOC conversion was mainly due to the loss of GAC basic sites upon ozonation [20–22]. In addition, the formation of acidic SOG on the entrance of micropores and the decrease of PZC might prevent the adsorption of organic compounds (i.e., gallic acid and ozonation by-products) onto the GAC to some extent, thereby contributing to decrease the overall effectiveness of the catalytic system.

3.2.2. GAC/ O_3 -regeneration experiments

First, a series of four GAC/ O_3 -regeneration experiments were carried out to find the optimum dose of ozone required to regenerate the spent GAC. After each experiment, the gallic acid adsorption isotherm of a sample of the regenerated GAC was obtained. Fig. 5 shows the isotherms of the virgin GAC and those regenerated with different amounts of ozone. All isotherms of Fig. 5 could be fitted by the Langmuir equation to get the parameters listed in Table 1. The average efficiency of regeneration was calculated following a

Table 2

Some properties of virgin GAC and after its use in consecutive catalytic ozonation and GAC/ O_3 -regeneration experiments to degrade either gallic acid or the WWTP effluent.

GAC sample	S_{BET} (m^2/g)	V_1 (cm^3/g)	V_2 (cm^3/g)	Acidic SOG ($\mu\text{equiv./g}$)	Basic SOG ($\mu\text{equiv./g}$)	PZC	Ash (%)
Virgin sample	710	0.16	0.51	792	196	6.3	16.2
Used sample 1	685	0.14	0.54	924	123	5.5	15.9
Used sample 2	643	0.11	0.59	1143	75	5.1	16.4
Used sample 3	579	0.08	0.56	1478	44	4.7	15.1

Used sample 1. GAC sample used in four consecutive catalytic ozonation experiments to degrade gallic acid. Used sample 2. GAC sample used in a four-cycle GAC/ O_3 -regeneration experiment to degrade gallic acid. Used sample 3. GAC sample used in a three-cycle GAC/ O_3 -regeneration experiment to degrade the WWTP effluent.

method that compares the entire Langmuir isotherms of virgin and regenerated GACs. For that purpose, Eq. (5) was used:

$$PR(\%) = \frac{q_{m,R} \cdot K_{L,R}}{q_{m,V} \cdot K_{L,V}} \times \frac{1}{N} \sum_{i=1}^N \frac{1 + K_{L,V} \cdot C_{e,i}}{1 + K_{L,R} \cdot C_{e,i}} \times 100 \quad (5)$$

where the subscripts V and R refer to virgin and regenerated GACs, respectively. For the computation, 300 values of $C_{e,i}$ (i.e., $N = 300$) were taken regularly distributed from 1 to 301 mg/dm³. Table 1 gives results for the amount of ozone consumed for GAC regeneration, expressed both per unit mass of GAC (D_{O_3}) and per unit mass of TOC adsorbed (η_{O_3}). Eqs. (6) and (7) were used to calculate these ozone consumptions:

$$D_{O_3} = \frac{F_g \cdot \int_0^{t_R} (C_{O_3,i} - C_{O_3,o}) \cdot dt}{w} \quad (6)$$

$$\eta_{O_3} = \frac{D_{O_3} \times w}{2.24 \cdot F_l \cdot \int_0^{t_A} (C_{GA,i} - C_{GA,o}) \cdot dt} \quad (7)$$

where F_g is the gas flow rate; $C_{O_3,i}$ and $C_{O_3,o}$ are the concentrations of ozone at the ozonation chamber inlet and outlet, respectively, during the regeneration stage; w is the dry mass of GAC used in the experiments; F_l is the liquid flow rate; $C_{GA,i}$ and $C_{GA,o}$ are the concentrations of gallic acid at the adsorption column inlet and outlet, respectively, during the adsorption stage; t_A and t_R are the durations of the adsorption and regeneration stages, respectively. The coefficient 2.24 was used to convert the mass of gallic acid into the equivalent mass of carbon atoms. As shown in Fig. 5 and Table 1, the adsorption capacity of the GAC for gallic acid decreased after any GAC/ O_3 -regeneration experiment. Nevertheless, sample O_3 -Reg-0.4 (i.e., $D_{O_3} = 0.42$ g O_3 /g GAC) exhibited larger regeneration efficiency (PR), maximum adsorption capacity (q_m) and adsorption affinity (K_L) than the other ozone-regenerated samples, suggesting that there is an optimum dose of ozone to recover most of the original GAC adsorption capacity for gallic acid. An attractive feature of the GAC/ O_3 -regeneration experiment at optimum conditions is the efficient use of ozone. Thus, η_{O_3} was as low as 6.2 g O_3 /g TOC, which is even lower than the consumption measured in the catalytic ozonation experiment discussed in the previous section (i.e., 7.4 g O_3 /g TOC).

Ozone-regeneration is intended to completely oxidize the adsorbed compounds without altering the porosity and surface chemistry of the GAC. However, experimental results in this work show that the process was not successful at the recovery of all the adsorption capacity of the virgin GAC. Regeneration efficiencies below 100% in Table 1 suggest: (i) failure of ozonation to remove all the adsorbates from the GAC surface and/or (ii) destruction of adsorptive sites and plugging of pores. In an attempt to further investigate the reasons of incomplete regeneration, some ozone-regenerated samples were analyzed for thermal desorption of adsorbed compounds and surface characteristics. Fig. 6 shows the differential thermogravimetric (DTG) profiles for the virgin GAC, a spent GAC saturated with gallic acid and three ozone-regenerated GACs. The small bands observed in the DTG curve of the virgin GAC can be due to thermal decomposition of different SOG [23]. Two peaks at about 150 and 300 °C can be observed in the DTG curve of the spent GAC, which can be assigned to the release of physisorbed and chemisorbed gallic acid, respectively [24]. Both peaks can also be seen, though they are much weaker (note the change in Y-axis scale), in the DTG curve of the GAC regenerated with the lowest ozone dose (i.e., sample O_3 -Reg-0.1). These peaks are shifted towards lower temperatures in the DTG curves of samples O_3 -Reg-0.4 and O_3 -Reg-0.6. This result suggests that the amounts of gallic acid on these samples were lower than that in sample O_3 -Reg-0.1

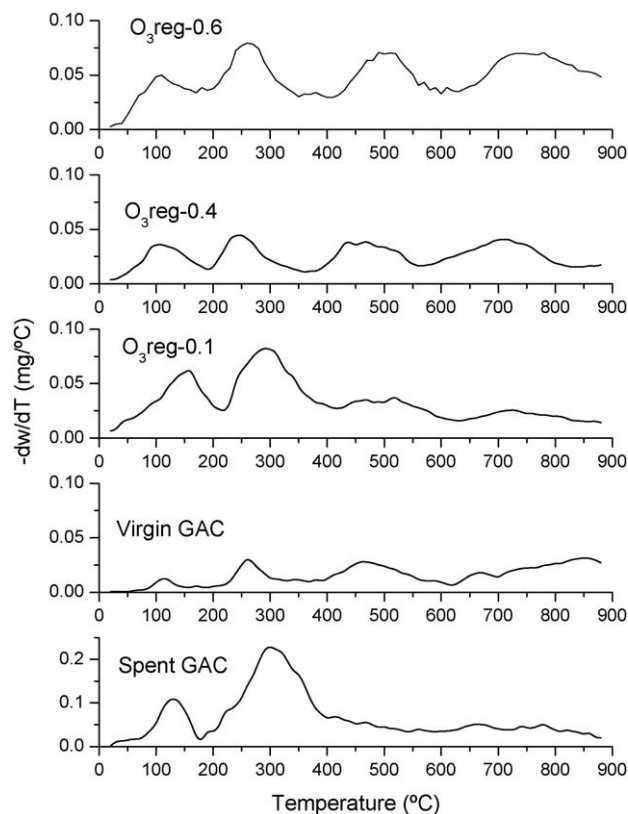


Fig. 6. TGA plots for virgin, spent and some ozone-regenerated GACs.

but other adsorbed species and SOG were present there in greater extents. The peak at about 110 °C can be assigned partly to loss of trapped water while the peak centred at about 250 °C can be mainly due to the decomposition of carboxylic groups formed from the reaction of ozone with gallic acid and the GAC surface. Other peaks in ozone-regenerated samples attributable to ozonation products are the peaks at about 400–550 °C that can be associated with the thermal release of anhydrides and lactones and the broad peak centred at about 750 °C that may represent the decomposition of different groups, including phenolic groups. A peak intensity analysis in Fig. 6 leads one to think that sample O_3 -Reg-0.4 is cleaner from adsorbed products and SOG than the surface of the GAC regenerated with the highest dose (i.e., sample O_3 -Reg-0.6). Table 3 shows some parameters of the porous structure of the virgin and regenerated GACs as calculated from adsorption of nitrogen data. It is clearly seen that the regeneration with ozone, if not applied at optimum conditions, produced a significant decrease in the surface area and the volume of micropores (V_1). The volume of mesopores (V_2) of any regenerated GAC was larger than that of the virgin GAC, likely as a consequence of the widening of microporosity produced by ozone [25,26].

Fig. 7 shows the gallic acid breakthrough curves generated from the results of a GAC/ O_3 -regeneration experiment comprising four consecutive adsorption–regeneration cycles. Care was taken to keep the amount of ozone consumed at each regeneration stage

Table 3
Some textural properties of virgin and some ozone-regenerated activated carbons.

GAC sample	S_{BET} (m ² /g)	V_1 (cm ³ /g)	V_2 (cm ³ /g)
Virgin sample	710	0.16	0.51
O_3 -Reg-0.1	502	0.05	0.58
O_3 -Reg-0.4	697	0.14	0.62
O_3 -Reg-0.6	601	0.10	0.65

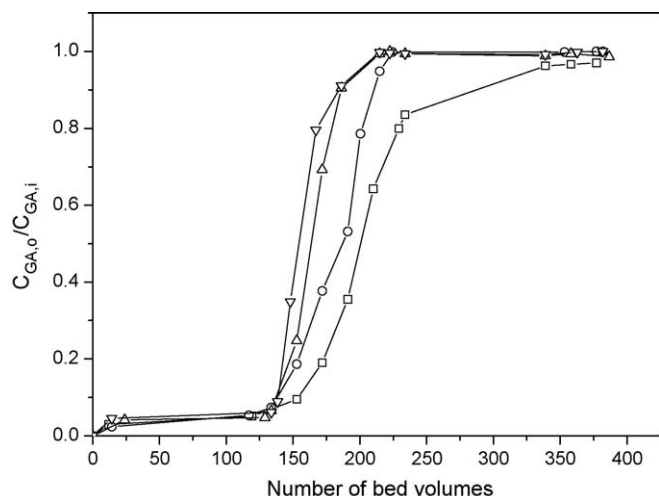


Fig. 7. Gallic acid breakthrough curves from the dynamic adsorption stages of a four-cycle GAC/O₃-regeneration experiment. Symbols: □, first cycle; ○, second cycle; △, third cycle; ▽, fourth cycle.

close to the optimum 0.42 g O₃/g GAC. Fig. 7 reveals a progressive shift of the breakthrough curves to the left as far as the number of cycles was increased. This result is not surprising as incomplete GAC regeneration was expected to be achieved with ozone. The overall amount of gallic acid adsorbed onto the GAC during each dynamic adsorption stage decreased gradually as follows: 320 mg/g GAC (first cycle), 277 mg/g GAC (second cycle), 253 mg/g GAC (third cycle) and 240 mg/g GAC (fourth cycle). However, the initial breakthrough was almost coincident in the four dynamic adsorption stages at about 125 bed volumes. Considering the whole experiment (four cycles), the average specific ozone consumption was calculated to be 7.4 g O₃/g TOC degraded. This figure is even lower than the average consumption of ozone in the four consecutive catalytic ozonation experiments (see Section 3.2.1) which was 8.2 g O₃/g TOC degraded. A sample of the GAC used in the four-cycle experiment was analyzed for porous and chemical surface properties. The results are those in Table 2 corresponding to Used sample 2. From this table it can be seen that the GAC surface changed in the same way after the four consecutive O₃/GAC experiments and the four-cycle GAC/O₃-regeneration experiment: some destruction of porosity, fixation of acidic SOG, removal of basic SOG and decrease of PZC. However, it should be noted that these changes were more pronounced in the GAC/O₃-regeneration experiment. They can explain the lowering in the GAC adsorption capacity for gallic acid. First, there is less surface available for adsorption. Second, the mentioned changes in SOG leads to removal of π electrons from the basal planes of carbon, thus weakening the dispersive interactions through which gallic acid adsorbs. Third, the decrease of PZC increases the polarity of the surface and favors the selectivity of adsorption towards water [26].

3.3. Degradation of a secondary effluent from a WWTP

A complete characterization of the WWTP effluent used in this work is given in Table 4. It is worthy to note that it had a large content of organic matter as deduced from the high COD and TOC values, which means that the secondary treatment applied at the WWTP failed to achieve proper wastewater purification. Therefore, further treatment is needed before discharge or reuse.

Fig. 8 shows some temporal profiles of normalized TOC during single ozonation, single adsorption and catalytic ozonation experiments treating the WWTP effluent. It should be stated here that the removal of COD in all these experiments (not shown) was

Table 4

Quality summary of the WWTP effluent used in this work.

Parameter	Mean value \pm S.D.
pH	6.12 \pm 0.50
Conductivity (mS/cm)	11.44 \pm 0.75
Total suspended solids (g/m ³)	321 \pm 36
Volatile suspended solids (g/m ³)	220 \pm 21
COD (g/m ³)	522 \pm 55
BOD ₅ (g/m ³)	150 \pm 100
TOC (g/m ³)	171 \pm 12
IC (g/m ³)	27 \pm 6
Polyphenols (g/m ³) ^a	26 \pm 5
P-PO ₄ ³⁻ (g/m ³)	3.0 \pm 0.2
N _T (g/m ³)	16.8 \pm 1.1
N-NH ₄ ⁺ (g/m ³)	14.0 \pm 0.8
UV absorbance (254 nm) ^b	0.40 \pm 0.03

^a As gallic acid.

^b Measured on samples diluted five times.

not different from the removal of TOC. In Fig. 8, it can be clearly observed that the secondary effluent was very refractory to single ozonation as less than 25% TOC removal was achieved in 2 h of exposure to ozone. The removals of TOC and COD by single adsorption onto GAC were also limited to around 40%, which is in agreement with the equilibrium results shown in Fig. 2B. TOC and COD degradations were enhanced by the simultaneous use of ozone and GAC. Thus, for example, about 50% and 60% of TOC removals were achieved within 2 h in experiments carried out with 2 and 5 g of GAC, respectively. From Fig. 8 it is also apparent that the GAC did not suffer appreciably deactivation towards TOC degradation even after its third use, since the TOC profile did not vary with the repeated use of GAC. Regarding specific ozone consumption, in the single ozonation experiment it was found to be 18.8 g O₃/g TOC degraded but it markedly decreased up to 9.6 g O₃/g TOC (average value) in the catalytic ozonation experiments.

A GAC/O₃-regeneration experiment comprising three adsorption–regeneration cycles was carried out to treat the WWTP effluent. The amount of ozone consumed at each regeneration stage was about 0.35 g O₃/g GAC. Fig. 9 shows the COD breakthrough curves.

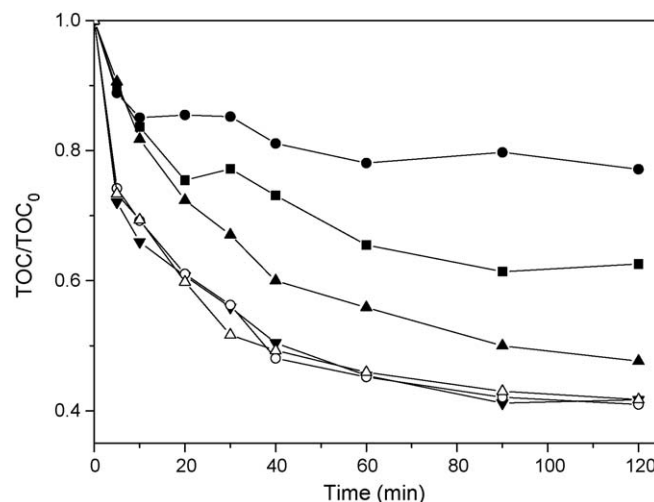


Fig. 8. Degradation of WWTP effluent by single adsorption, single ozonation and catalytic ozonation experiments. Reaction conditions: $T \approx 20$ °C; pH = 6; aqueous solution volume = 250 cm³; initial TOC \approx 170 g/m³; recirculation flow rate = 2 dm³/h; GAC weight (if applied) = 2 g; gas flow rate = 25 N dm³/h; ozone concentration at the gas inlet \approx 40 g O₃/m³. Symbols: ■, adsorption experiment; ●, single ozonation experiment; catalytic ozonation experiments: ▲, GAC weight = 2 g, fresh GAC; ▽, GAC weight = 5 g, fresh GAC; ◇, GAC weight = 5 g, one-time reused GAC; △, GAC weight = 5 g, two-time reused GAC.

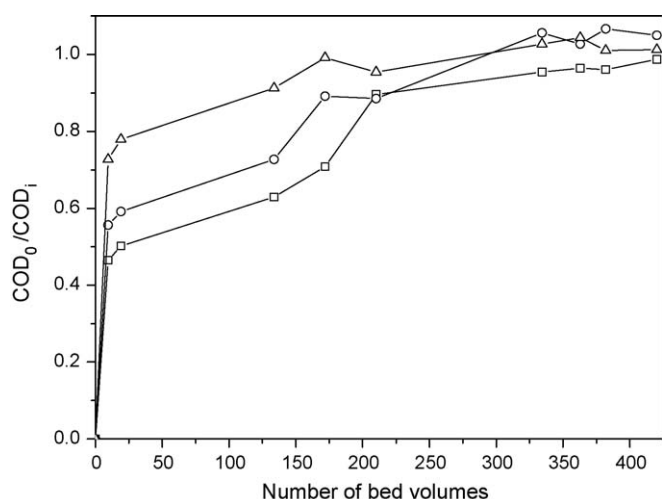


Fig. 9. WWTP effluent breakthrough curves from the dynamic adsorption stages of a three-cycle GAC-O₃-regeneration experiment. Symbols: □, first cycle; ○, second cycle; △, third cycle.

As can be seen, the column effluent had large COD values from the beginning of the adsorption stage. This result confirmed that a substantial fraction of COD of the WWTP effluent was not amenable to adsorption onto this GAC. The non-adsorbable COD fraction increased with the number of cycles, suggesting that the regeneration with ozone destroyed adsorption sites. Table 2 shows textural and chemical surface properties of a GAC sample after being used in this three-cycle experiment (Used sample 3). Destruction of porosity and modification of surface chemistry (i.e., fixation of acidic SOG, removal of basic SOG and decrease of PZC), because of ozone regeneration, are evident from results. All these findings suggest that only a minor fraction of the surface was covered by adsorbates in the spent GAC. Thus, at regeneration stages, ozone reacted mainly with the GAC itself producing loss of porosity and chemical oxidation of the surface making it more hydrophilic. As a consequence, ozone-regeneration induced changes in the GAC adsorption properties.

4. Conclusions

Catalytic ozonation using GAC as a catalyst is an AOP proved to be effective to degrade aqueous gallic acid and a secondary effluent from a full-scale WWTP. Major benefits of catalytic ozonation in comparison with single adsorption and single ozonation were faster degradation, higher degree of mineralization and better use of ozone. The GAC used in this work showed some minor deactivation towards gallic acid degradation with its repetitive use in ozonation experiments. Deactivation can be attributed to surface ozone reactions that gave rise to the fixation of acidic SOG and the removal of basic SOG. As a result, the GAC became more hydrophilic (lower PZC) thus affecting its adsorption behaviour and its ability to decompose aqueous ozone into secondary oxidants (i.e., hydroxyl radicals). No deactivation was observed after three uses of the GAC in catalytic ozonation experiments treating the WWTP effluent. Therefore, the treatment stands out as a significant candidate to be considered for full-scale operations.

Dynamic adsorption onto GAC followed by ozone-regeneration of spent GAC (i.e., GAC/O₃-regeneration process) can be a useful method to treat wastewater with high concentration of adsorbable compounds that react fast with gaseous ozone, as it is the case of gallic acid. However, even in this case, regeneration efficiencies lower than 90% were obtained at the conditions of this work. The GAC/O₃-regeneration method failed to efficiently remove COD from the WWTP effluent as a substantial fraction of organic matter did not adsorb onto the GAC. The process also failed to regenerate the GAC as ozone destroyed its texture and reduced its surface basicity to significant extents.

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